

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
December 24, 2001

3. REPORT TYPE AND DATES COVERED
Final Report. 1 April 2000-31 March 2001

4. TITLE AND SUBTITLE

Scanning Force microscopy of Nanostructured Conducting Composites and Polymeric Materials.

5. FUNDING NUMBERS

Proposal Number P-40831-MS-RIP
Grant Number DAAD19-00-1-0033

6. AUTHOR(S)

Dr. Tito E. Huber, Howard University Professor

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Howard University

8. PERFORMING ORGANIZATION
REPORT NUMBER

Howard University 634325 Report Number 2

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING
AGENCY REPORT NUMBER

40831.1-MS-RIP

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT

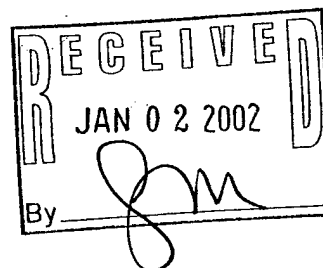
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The Scanning Probe Microscope at Howard University is functional. The SPM is a centerpiece in the laboratory of Professor Huber. The AFM is used in the performance of the grant DAAD 19-99-1-0282 for the testing and fabrication of nanostructured thermoelectric materials and devices based in Bi and Bi-Sb alloys. These materials are sought for thermoelectric applications at around 100 K, such as detector coolers and cryogen shields. The report itemizes other grants and proposal based on the AFM and purchase details. The report also describes activities such as training of students, a new course being developed and offered. The report also presents research results: Optical Microscopy and electric Force Characterization of a Bi nanowire, AFM and living cells (with Dr. Palmer a co-investigator in the original proposal), and the research in Bi nanowires. Finally, the report presents a list of collaborators involved in making the instrument into a true research facility.

20020125 289



14. SUBJECT TERMS

AFM, SPM, EFM

15. NUMBER OF PAGES

14

16. PRICE CODE

17. SECURITY CLASSIFICATION
OR REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION
ON THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION
OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

Final Report:

Agency DOD/ARO

DAADI9-00-1-0033

Award Amount: \$122,795

Cost Sharing: \$20,000 from the Department of Chemistry (\$10,000) and the Office of Research Administration (\$10,000) at Howard University.

Total cost of Performance: \$142,795.

Funds have been spent (\$138,895) or obligated for specific purchases (\$3,900) related to the microscope.

The atomic force microscope at Howard University is based in the Laser Chemistry Laboratory of the Department of Chemistry. The laboratory address is 500 College St. N.W. PI is Prof. Huber. Co-investigators are Prof. Pollack and Prof. Palmer. Professor Pollack is currently on a sabbatical leave. Prof. Palmer moved to Notre Dame University.

Our plan is to make this equipment a feature in many research activities at Howard University. To this end we started many collaborations that are about to come into fruition. We are against allowing external users access to the equipment. In this report I emphasize the work in collaboration with other researchers at Howard. This work will guarantee the continuation of the use of the SPM and provides a support base for it.

The equipment is based in a Multimode Scanning Probe Microscope and a Nanoscope III system controller manufactured by Digital Instruments, Santa Clara, CA. Digital Instruments is a subsidiary of Veeco Inc. This instrument is designed for high resolution. It can render topographic images as well as allowing for the measurement of position dependent forces, such as electrical forces due to local electric fields.

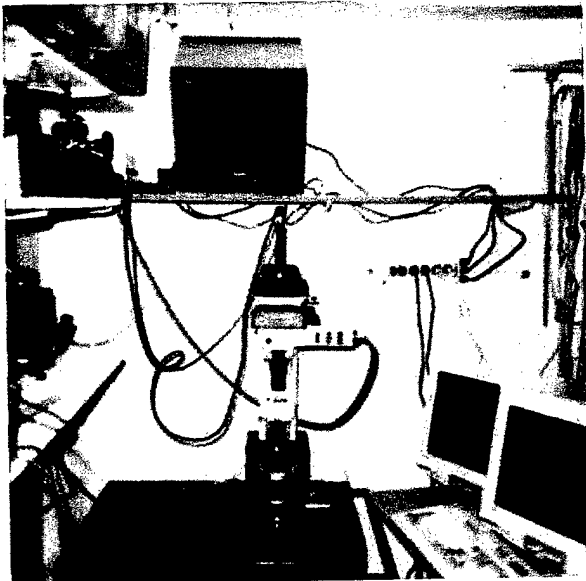


Fig. 1. Photograph of the AFM at Howard University. This layout has been improved since this picture was taken. The SPM microscope proper is the metal cylinder in the center of the picture under the binocular optical microscope. The SPM proper is resting on a sturdy metal table. On the left, the monitors of the Nanoscope III controller. On the top right the video monitor that outputs the optical microscope image. This video signal is fed back in the computer for documentation purposes.

OTHER GRANTS AND PROPOSALS

The Howard U. SPM can be employed in many projects. We are participating in many proposals to funding agencies:

- a) Army Research Office grant DAAD4006-MS-SAH
- b) NSF grant entitled "Template Synthesis and Electronic Properties of Bi quantum Wire Arrays and Networks", NSF Award # 0072847.
- c) NASA grant entitled Nanocomposite-Based Compact Thermomagnetic Cryocoolers. NASA Grant Number NAG5-10371
- c) NSF-Research in Undergraduate Institutions NSF-0097733. (Funded 2000)
- d) NSF-Centers for Research Excellence in Science and Engineering (Submitted November 2001). Principal Investigator is Dr. Lecca, Dean of Pharmacy and Allied Sciences. This is a large (multi-million dollar) project including infrastructure for atomic force microscopy.
- e) NSF Nanoscale Science and Technology. Nanoscale Interdisciplinary Team. Submitted Dec. 19, 2001. Proposed PI is Dr. G. Harris of Electrical Engineering P.I.. "Electrical Properties of GaN nanowires".

PURCHASE DETAILS

At the time that I was deciding about the equipment there were two companies: Digital Instruments (DI) and ThermoMicroscopes. These companies had very similar equipment and it took a few months to arrive to a decision. The reason that it was so time consuming is that the companies arranged for demonstrations (in their site) of their equipment and I had to decide the best equipment for my application. The equipment demonstrated by ThermoMicroscopes had some features that were better than DI but, overall, DI had a better product:

Good features of ThermoMicroscope: High-z span of 15 microns whereas DI only moves 5 microns.

Uses competitive, third party lock-in.

Easy of set-up.

Good features of DI/ Veeco equipment:

High Resolution.

Very difficulty to set-up a new sample. Samples have to be prepared very flat and induce the operator to continue to work with the same sample for more in-depth experiments.

Software more proven.

The optical microscope that is an integral part of the SPM is superior. However, this particular Nikon microscope is not standard (Uses third party components) and parts for

it are difficult to locate. Nikkon has very little interest in support; they appeared to be very interested in just selling complete microscopes but not the little parts for it. Support is very important: DI appeared to be more stable financially. This is confirmed: Thermomicroscopes is out of business now.

ACTIVITIES: TRAINING OF STUDENTS

We trained a number of students in the use of the SPM.

S. Solomon. Graduate student at Howard University

Rich Messer, summer 2001 student under RUI (NSF).

Kizi Celestine, undergraduate student at Howard University.

New course at Howard University:

I developed a course of microscopies centered on the SPM. I taught the course on SPM's to students. Only a few students can be trained in this equipment at a time because it is difficult to set-up and there are many things that can be misaligned or broken by an inexperienced operator. So this course is very time consuming. I think that such a course should be developed around a special training SPM (like the basic Explorer from Thermomicroscope) rather than the main SPM.

New Course: Scanning Probe Microscopy

Course description: This course is intended for chemistry, physics, engineering, and health sciences undergraduate and graduate students seeking to understand the concepts, instrumentation, and applications of SPM. Examples of SPM will be covered extensively in both lecture and laboratory sessions while more recent techniques will be covered in varying depths depending on the interests of the students. Lectures will be supplemented by lab sessions using a Digital Instruments Nanoscope III.

Theory of operation and quantification of data will be addressed with attention paid to instrumental artifacts and methods to avoid them.

We will also look at probe tip technology, SPM modes, tip-sample interactions. Graduate students will be encouraged to bring their own samples.

When: Tentatively, we are planning to meet every Wednesday at 6 PM for two hours.

Course literature: Extensive notes of all lecture materials will be provided as a course notebook.

Organizer: Professor Tito Huber, Department of Chemistry
Students interested in this course please email me at thuber@howard.edu.

Reference materials at www.di.com

ACTIVITIES: RESEARCH RESULTS

I. Optical Microscopy and Electric field Force Characterization of a Bi Nanowire

T.E. Huber and P. Zhou, Laser Chemistry Laboratory, Howard University, Washington, DC 20059, USA

And A. Nikolaeva, Institute of Applied Physics, Moldova National Academy of Sciences, 5 Academy Str., MD 2028 Kishinau, Moldova. Travel by A. Nikolaeva under the auspices of the Cobase program of the National Research Council.

Abstract

We have measured the electrical continuity of a Bi microwire embedded in a glass matrix. The method is based in a Digital Instruments Scanning Probe Microscope with electric force capabilities. This equipment measures the electric field gradient distribution above the sample surface using a double pass technique; the first pass measures the sample topography profile and the second pass images the electrical force experienced by the SPM tip while maintained at a fixed distance from the sample.

The following sample was prepared

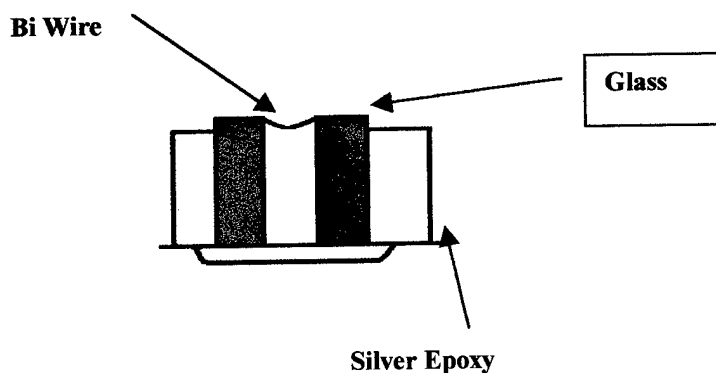


Fig 2. Sample layout

The sample was characterized utilizing a Scanning Electron Microscope of the Department of Electrical Engineering at Howard University.

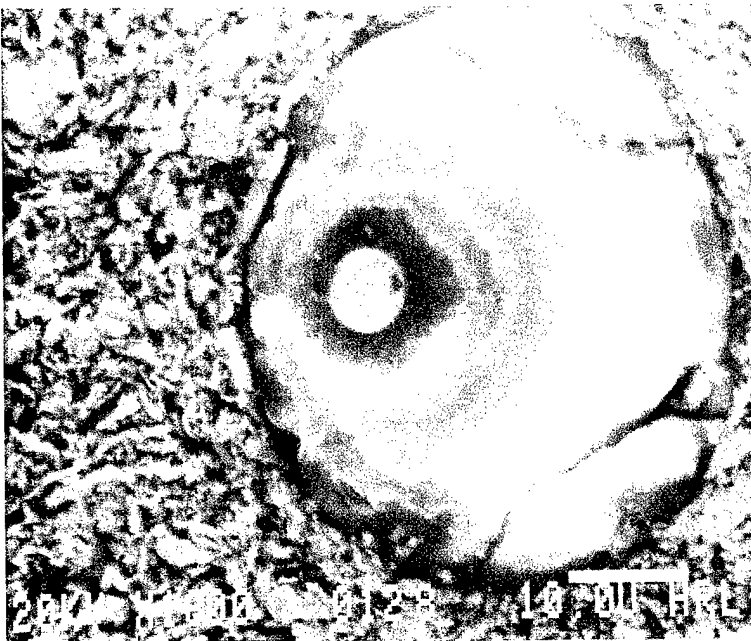


Fig. 3 A SEM image of a Bi microwire embedded in a glass fiber. The wire diameter is approximately $6\mu\text{m}$. The glass envelope shows a crack. The large grain material around the glass fiber is silver epoxy.

AFM: Topography and electric field

The nanowires composites create substantial electric field patterns over the sample surface. We used a scanning probe microscope to measure electric fields at the surface of a nanocomposite. In the scanning force microscope, the sample is mounted with conductive epoxy to a metal holder and is held at a few volts relative to a conductive cantilever tip that is grounded. The metal-coated, etched, single crystal silicon tip has a radius of curvature of about 5nm. The tip is set to oscillate at a frequency near its resonance frequency (78 kHz). When the cantilever encounters a vertical electric field gradient, the effective spring constant is modified, shifting its resonance frequency. By recording the amplitude of the cantilever oscillations while scanning the sample surface, we obtain an image that reveals the strength of the electric force gradient.

The image, however, may also contain topographical information; it is difficult to separate the two effects. This is circumvented by taking measurements in two passes over each scan line. On the first pass, a topographical image is taken with the cantilever tapping the surface, and the information is stored in memory. On the second pass, the tip is lifted to a selected separation between the tip and local surface topography (typically 20 to 200 nm), such that the tip does not touch the surface. By using the stored topographical data instead of the standard feedback, we can keep the separation constant. In this second pass, cantilever oscillation amplitudes are sensitive to electric force gradients without being influenced by topographic features. This two-pass measurement process is recorded for every scan line, producing separate topographic and electric force images. From these images, contours of electric force gradient can be drawn.

The amplitude of the cantilever oscillations is very large for small lift heights, and the images fade at separations larger than 80 nm. This is consistent with previous reports of a strong dependence of the tip-

surface force on the vertical separation. More work needs to be done to understand this feature quantitatively.

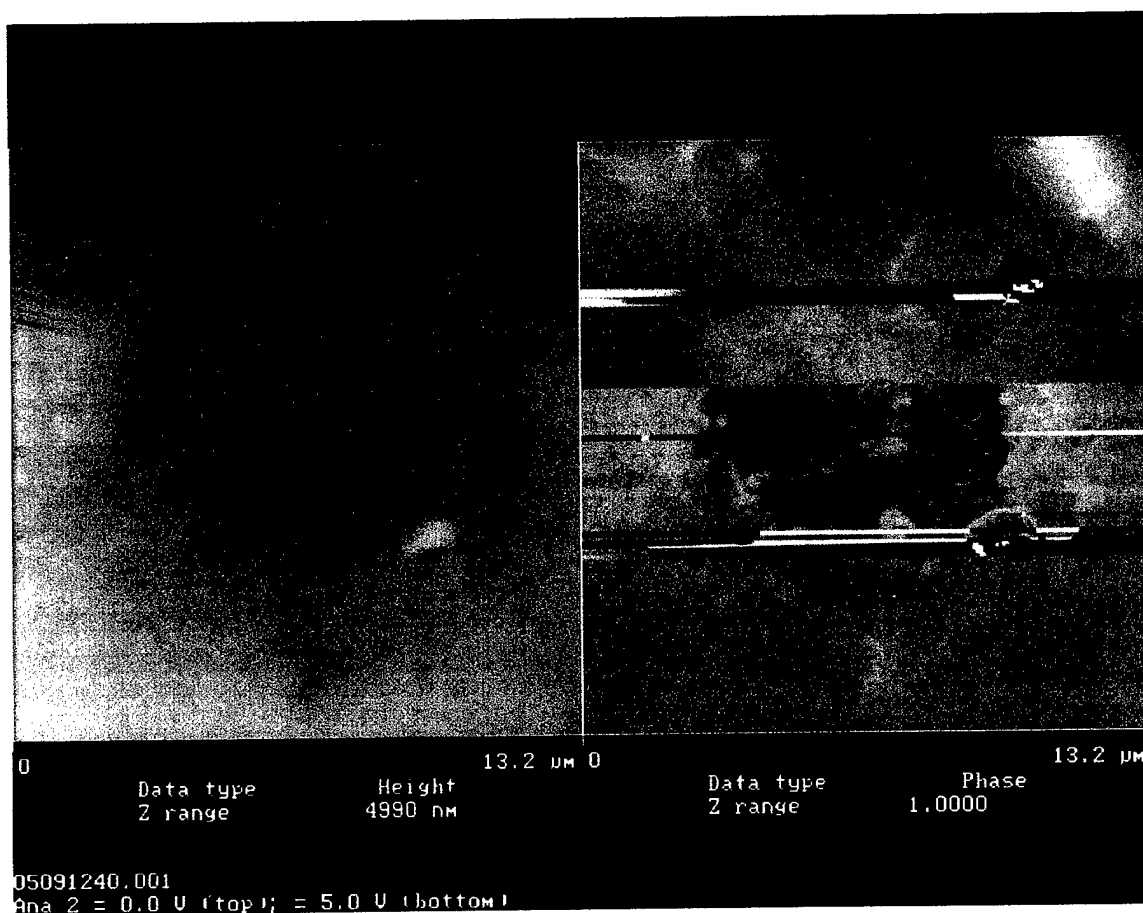
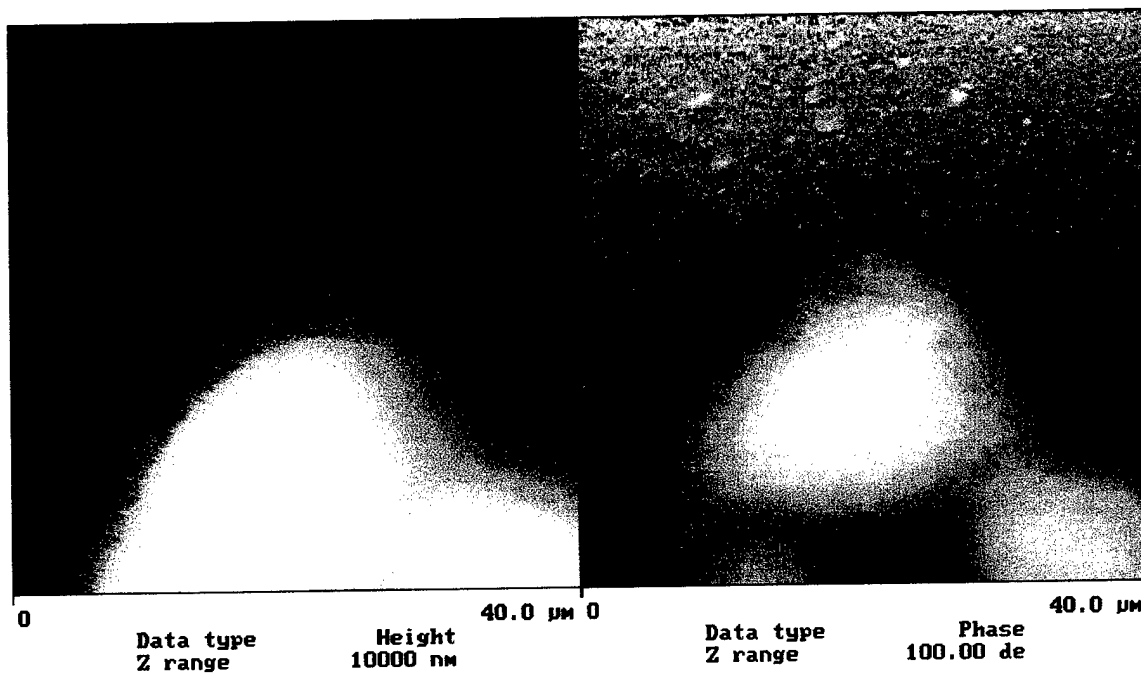


Fig. 4. Left: An SPM topographical image of the Bi microwire with an average diameter of $6 \mu\text{m}$. Right: An SPM phase image of the same portion of the microwire showing, in the bottom, the case of no electrical potential difference V between microwire and tip and, in the top, with $V=1 \text{ V}$. The horizontal lines in the left image are artifacts that we have since corrected. The picture presents evidence of a lack of calibration. This problem has been corrected.

II. SPM AND CELLS

We are working on a collaboration with Dr. A. Palmer of Chemistry researchers at the Faculty of Pharmacy at Howard University. They are interested in the effect of certain chemicals on living cells. The SPM is ideally suited for this purpose because the sample on cells on glass can be maintained in its buffer and are alive for days in the sample holder of the SPM. The cells themselves are cancer cells of the epithelium of the mouth of mice. This culture is grown and maintained in the facilities of the Department of Dentistry at Howard University. The cell line lasts indefinitely by allowing the cells to reproduce and multiply under the right temperature and culture media. A paper is being written on these investigations.



placebo.000

Fig. 5. This is the SPM view, topography and phase analysis of three live cells on glass. The cells are immersed in the fluid cell of the SPM. This cell allows for exchange of the buffer solution and in this way liposomes carrying chemicals can be placed in contact with the cells. This technique allows monitoring of the effect of these pharmaceutical chemicals on the cells in real time. In this case the glass bottom is covered with empty liposomes (100 nm in diameter). Therefore the name of the file; placebo.

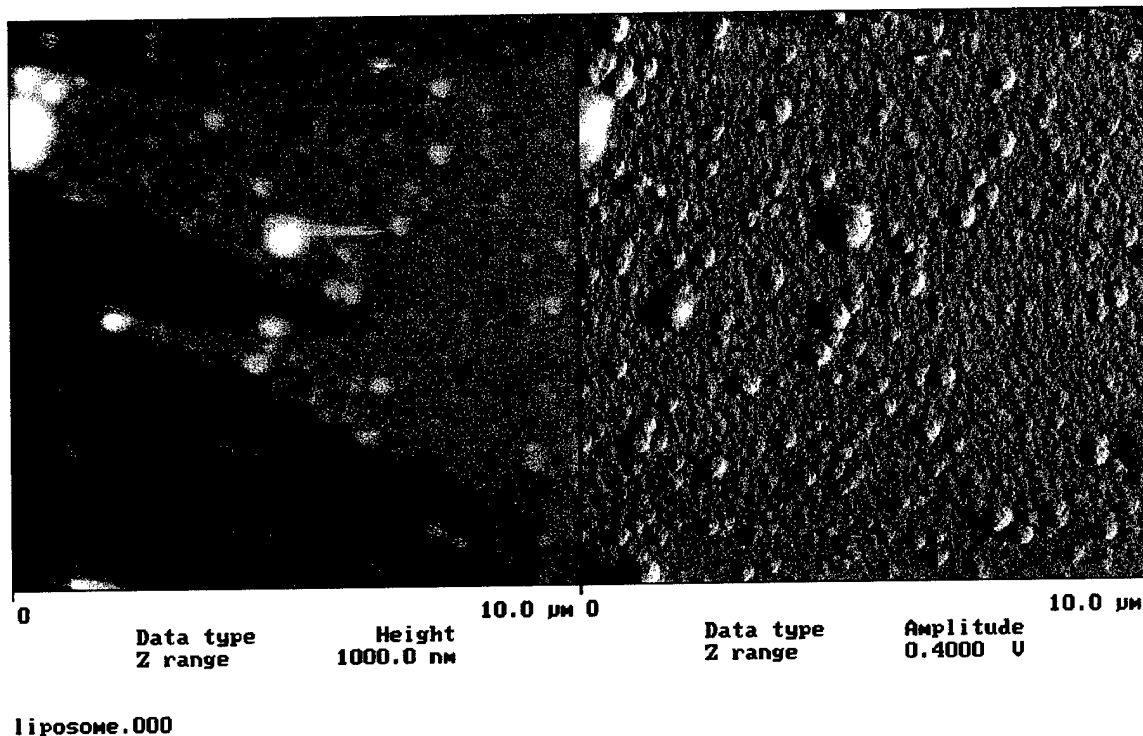
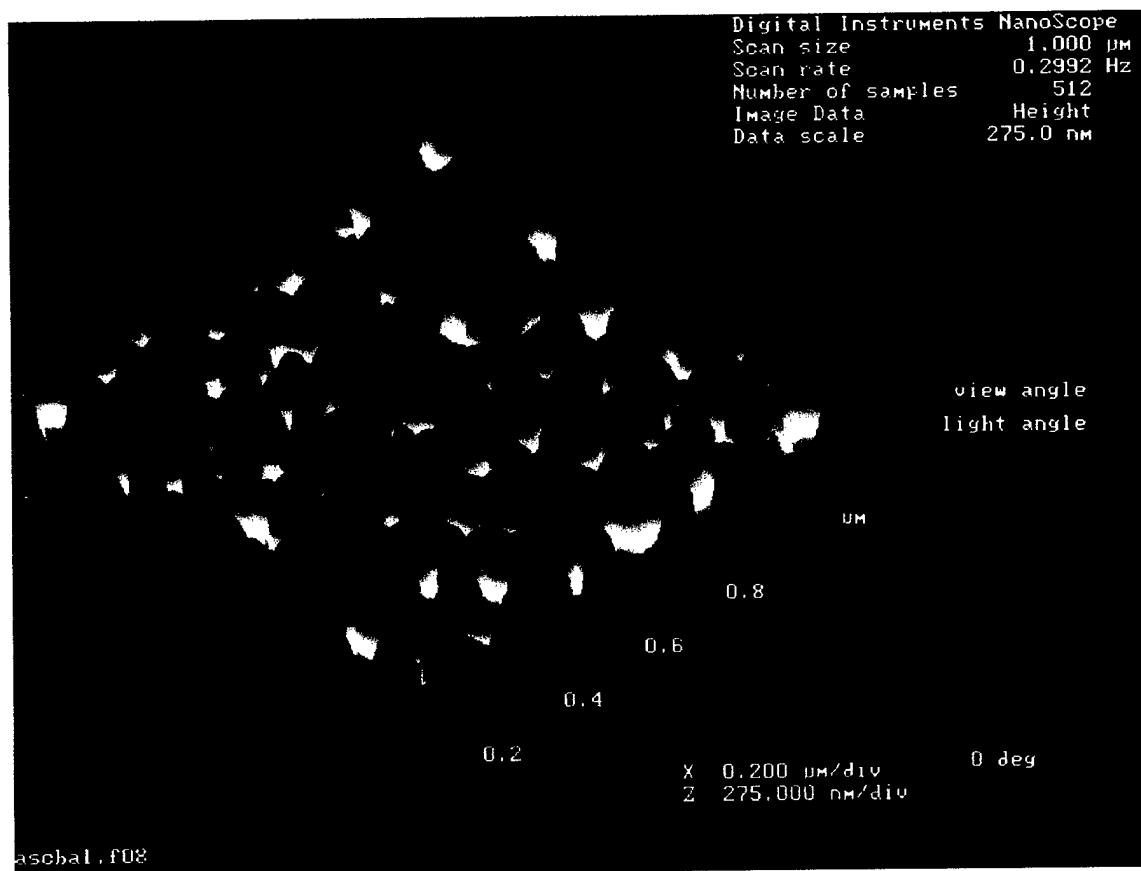


Fig. 6. This is a SPM view (topography and phase analysis) of the liposomes on the glass bottom of the SPM fluid cell. The liposomes are about 100 nm in diameter and are closed packed in many cases forming several monolayers. This is the reason that the cells in the picture on the cells show a mesa structure under the cells. This experiments require more refinement in the dose of liposomes in order to get good results and we are pursuing this work.

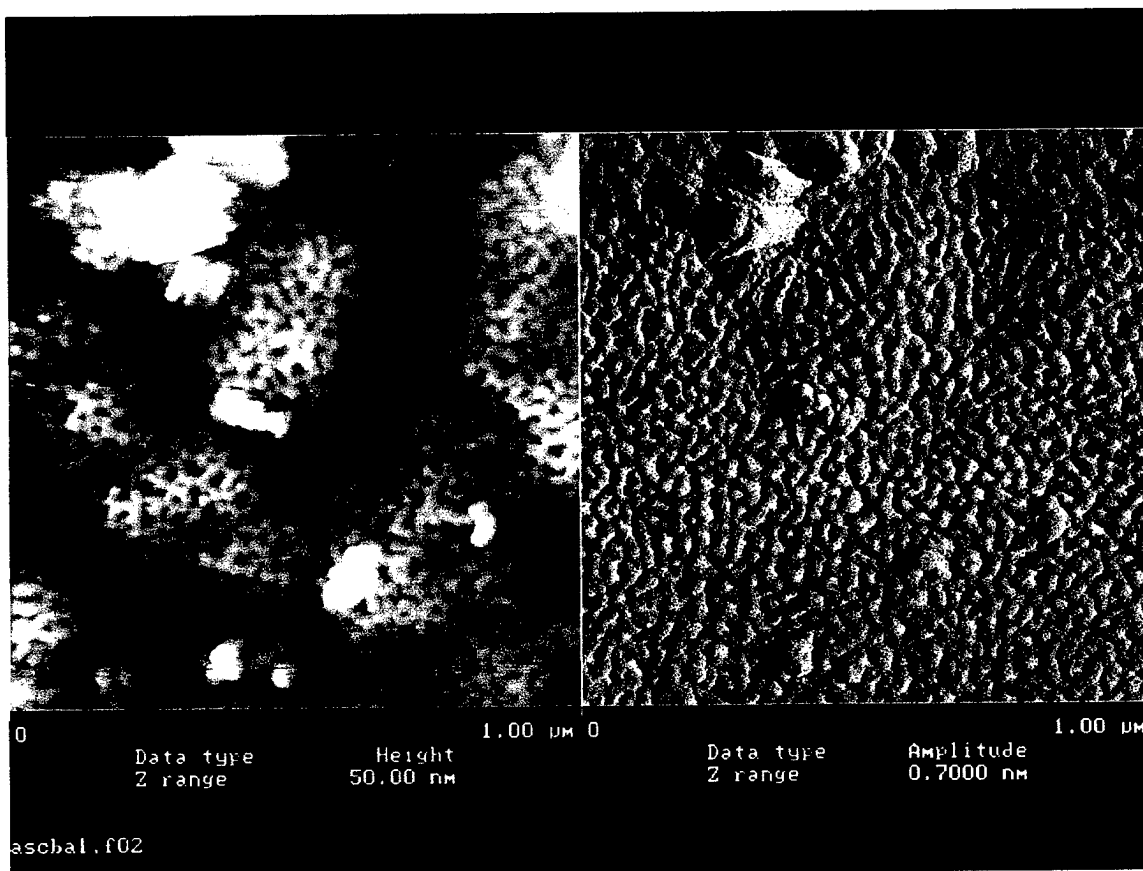
III. BISMUTH NANOWIRES.

This is our mainstream work. It involves the nanowire arrays prepared by high-pressure injection of the melt into porous alumina templates. The interest is this work is fundamental properties of quantum wires and application to thermoelectricity.

This is a AFM topographic image of 200 nm templates:



This is topographic image of the top view of our 30 nm templates. These templates have not being polished so that the texture of the surface is apparent. The right image is topography. The left image is phase imaging.



This is an optical image of the nanowire array between copper electrodes:

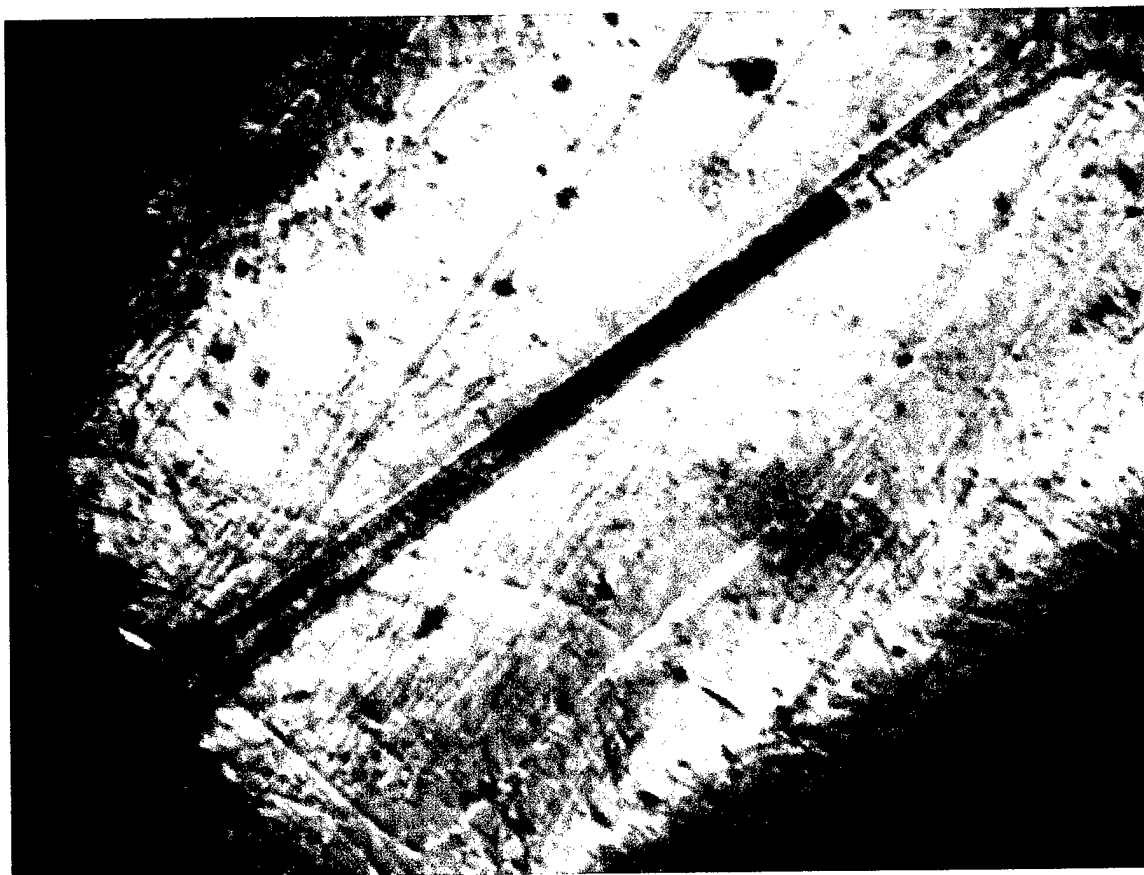


Fig. 7. Optical Micrograph of the 200 nm Bi wire array . The Bi wire array is the black area in the form of a thick line in the center of the picture. The red areas are two copper electrodes at either side of the sample. The area between the copper electrodes that shows a metallic shine is pure Bi.

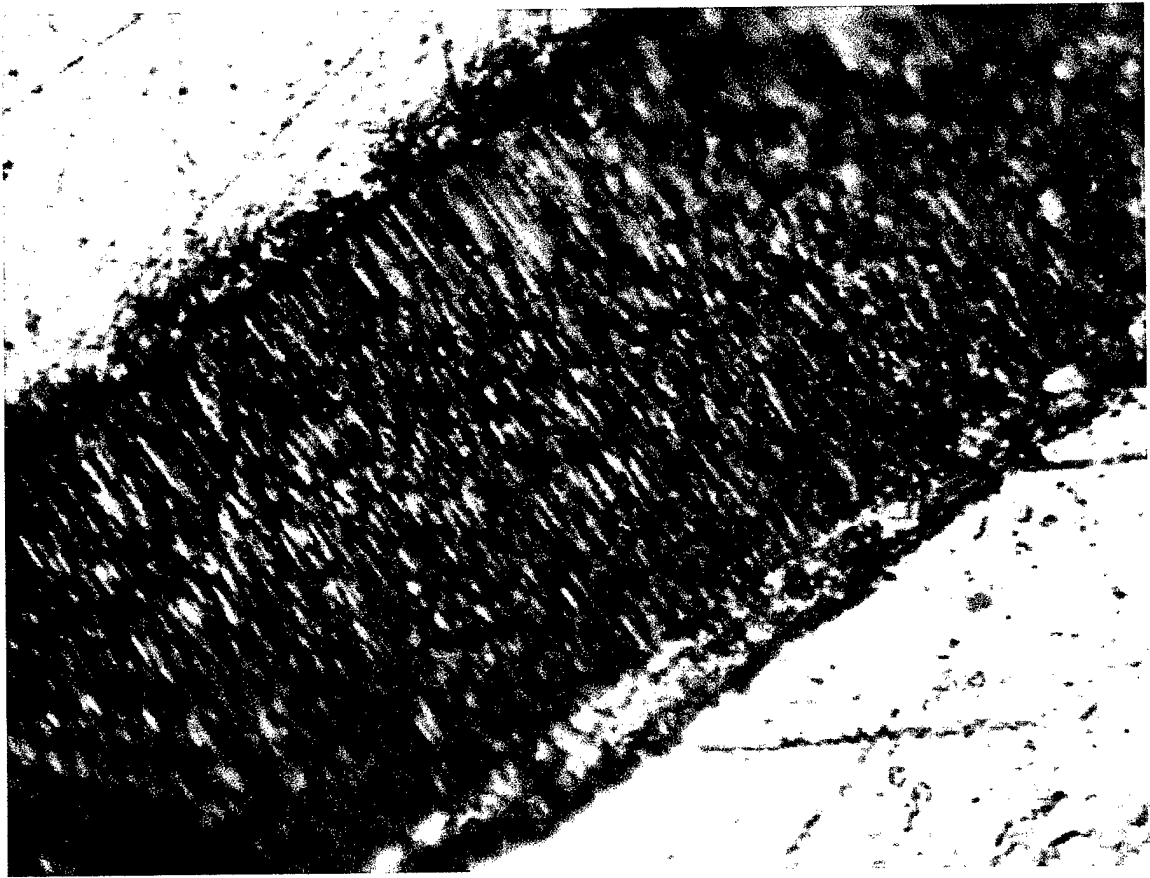
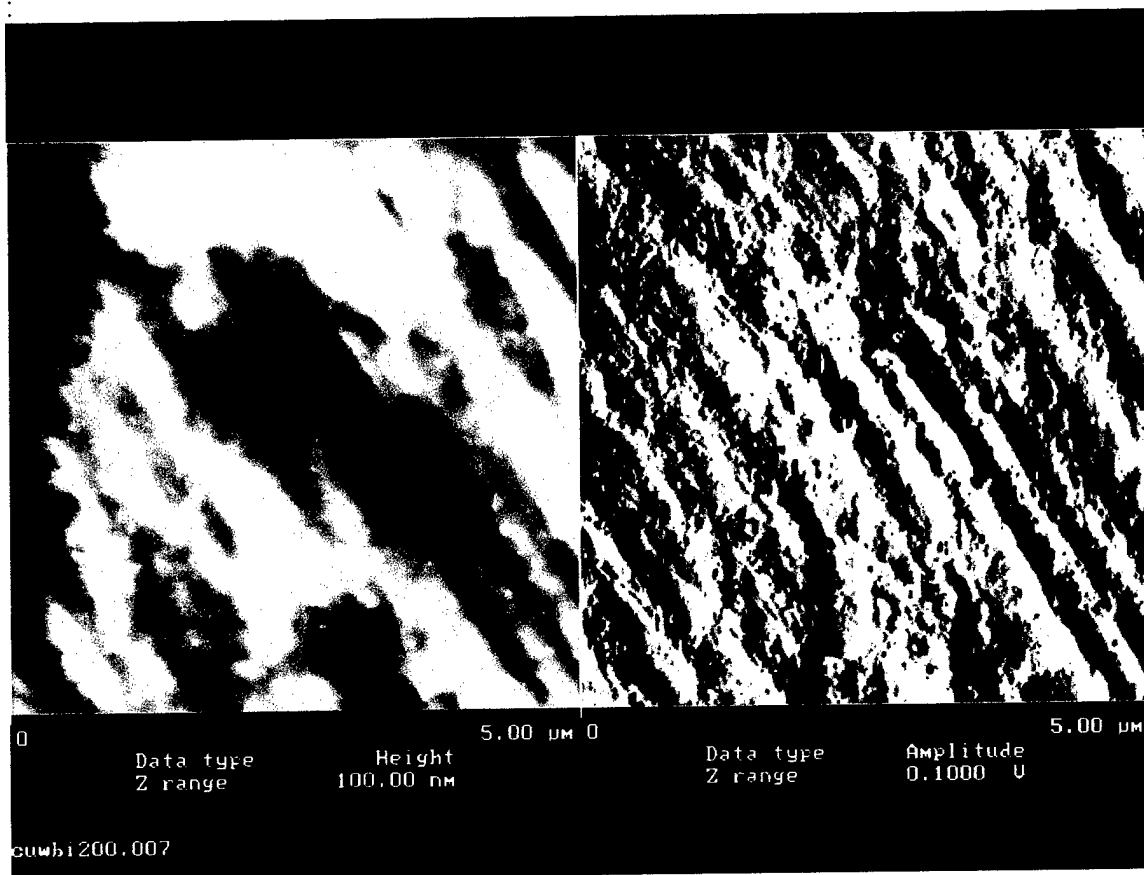


Fig.8 . Higher magnification view of the 200 nm Bi array between copper electrodes and Bi contact layers. This figure matches with the figure above. The wires can be seen in this picture.

We have studied this sample and many other samples of 200-nm and 30 nm Bi arrays with the SPM and the alumina templates that these composites are based on. The results of this work appear in publications being submitted to the Physical Review. A very raw image of the side of a 200 nm Bi nanowire follows. We are preparing better samples but the following image shows that we can image the Bi arrays. Again of the right the topography and on the left the phase image. In the future, we plan to etch the alumina surface of the samples in order to show better the nanowires



Work is being carried with SINGLE Bi nanowires and GaN nanotubes. This is an effort to show an electric field effect on the resistance of a single nanowires of Bi and GaN.

EQUIPMENT STATUS

The equipment is operational as I hope this reports demonstrates. Last pieces of instrumentation have already being ordered.

COLLABORATORS AND STUDENTS:

Prof. J. Catchings (Physics, Howard U. X-ray diffraction) ,
 Prof. Ray Butcher (Chemistry, Howard U., X-ray of single crystals)
 and A. Thorpe, Physics, Howard University. Magnetometer
 M.J. Graf, (Magnetoresistance) Boston College, Chestnut Hill, MA
 C.A. Foss, Jr, (Templates) Georgetown University, Washington, DC

Matt Erwin, (SEM analysis) Army Research Laboratory, Adelphi,
MD.

Albina Nikolaeva, (Magnetoresistance and single crystal work)
Academy of Sciences of Moldavia at Kishinev, Moldavia

Profs. S.Yamaguchi (Chubu U.), Y.Hasegawa, (Thermoelectric
properties, Saitama U.). Japan

Students:

At Howard University:

Keesha Hayes
Pierre Constant
Kizi Constantine
Tanisha Lucas
Miranda McDonald
Mr. S. Solomon